

A Study of the Nucleation Effect of Pigment Dyes on the Microstructure of Mass Dyed Bulked Continuous Filament Polypropylene

Hossein Tavanai*, Mohammad Morshed, Mohammad Zarebini, and
Ali Salehi Rezve

Textile Engineering Department, Isfahan University of Technology, Isfahan-84156, I.R. Iran

Received 4 May 2004; accepted 4 August 2004

ABSTRACT

The nucleation effect of 6 pigment dyes, namely: C.I. Pigment Yellow 83, Red 48, Blue 15, Violet19, Black 7 and White 6 on the microstructure of mass dyed BCF polypropylene i.e., crystallization temperature, melting point, percentage crystallinity, and birefringence has been studied by means of polarizing light microscope, DSC and FTIR. Tenacity and thermal shrinkage have also been studied. The results indicated that Yellow 83, Blue 15 and Black 7 act as monoclinic nucleating agents, whereas Violet19 and White 6 act as hexagonal nucleating agents. The nucleation effect of Red 48 seems to be negligible. Depending on the type of nucleation, the above mentioned parameters characterizing the microstructure of the fibres are affected. The birefringence of all coloured polypropylene fibres decreased as a result of pigment dyes added to the fibres. This leads to a reduction of the tenacity and thermal shrinkage of mass dyed BCF yarns.

Key Words:

polypropylene;
pigment dyes;
nucleation;
nucleating agent;
spherulite;
microstructure.

INTRODUCTION

Due to properties such as low production cost and energy consumption, ease of processing and recycling and excellent chemical resistance, polypropylene fibres have found extensive use as home, industrial and automotive textiles [1].

Polypropylene can be produced in isotactic, atactic and syndiotactic forms, from which only the isotactic form with a semicrystalline structure has the right properties for fibre production. Isotactic polypropylene, which is produced by the polymer-

(*)To whom correspondence should be addressed.
E-mail: tavanai@ac.iut.ac.ir

ization of propylene in the presence of Ziegler-Natta catalyst [1], crystallizes in monoclinic (α -phase), hexagonal (β -phase) and triclinic (δ -phase) forms. The monoclinic is stable at room temperature. The hexagonal form which appears in cold conditions, changes to monoclinic form easily. The hexagonal is also formed in polypropylene copolymers and in the presence of nucleating additives. J. Breda et al. [2, 3] have reported that with take-up speeds higher than 1350 m/min, any hexagonal form polypropylene will be replaced by monoclinic. The triclinic polypropylene with low stability is formed by crystallization at low quenching rate and high pressure [4].

Since the intermolecular attraction in polypropylene is limited to van der Waals forces, to ensure suitable physical properties, a relatively higher molecular weight (200,000-350,000) must be chosen for the fibre [1]. Due to the absence of suitable polar groups in its chemical structure, the unmodified polypropylene fibre cannot be dyed properly like other fibres. For this reason, mass dyeing (dope dyeing) is the only means for producing coloured polypropylene fibres. In mass dyeing, pigment dyes in the form of a master batch are mixed thoroughly with the molten polymer in the extruder. This colouration technique leads to very good overall fastness for polypropylene fibre. Pigment dyes may be organic or inorganic. Organic pigments have a higher colour strength, but a lower heat resistance in comparison to those of inorganic types. Chemical structure as well as particle size play important role in the shade, strength and brilliancy of pigment dyes [5].

The morphology (crystallinity and orientation) of polypropylene fibres is determined by the extrusion temperature, spinning speed, quenching conditions and the draw ratio applied during subsequent drawing. Crystallites known as spherulites are formed by the action of nucleating agents in nucleation process (formation of a nucleus) and the subsequent growth of lamella around it. Parallel molecular chains act as primary nucleating agent. Some additives as well as pigment dyes can also show nucleation properties; in other words act as nucleating agents and lead to crystallization occurring at higher temperatures [6-8] and the formation of a higher number of smaller spherulites. As the number of crystallization nuclei increases, so does the crystallization speed, the final percentage crystallinity and the number of spherulites [9, 12].

Controlling the crystallization in polymers with the help of nucleating agents has been investigated by many researchers [8,13,15]. Aromatic and aliphatic carboxylic acids, carbon black, kaolin, titanium dioxide, polydimethylstyrene, polyallyl xylene and aluminium, potassium, sodium and magnesium salts have been reported to act as nucleating agents for polypropylene [4]. Nucleating agents may be solids, liquids or gases. As an example, dispersed glycerine droplets and air bubbles can act as nucleating agents for polypropylene [9, 10]. It must be pointed out that the nucleation mechanism has not been very well understood yet. In polynucleation more than one nucleating agent is employed. This leads to a synergism effect for the nucleation. Some additives may act as nucleating agent for some systems and not for others. As an example, titanium dioxide acts as nucleating agent for polypropylene but not for polyethylene. Potassium stearate acts in the opposite way [13].

The following characteristics are necessary for the nucleating agents to act properly:

- Ability to lower the free surface energy between the polymers and additives.
- Insolubility in polymer and non-volatility.
- Higher melting point than polymer.
- Particle size between 1-10 micron.
- High dispersion homogeneity.
- Similar crystalline structure as polymer.

Morphi et al. showed that increasing the amount of titanium dioxide up to 0.5% as nucleating agent leads to a decrease in spherulite size of polypropylene [7]. Cramez et al. reported that some pigments can act as nucleating agent in polypropylene [16]. Zhu et al. reported that solid polypropylene can act as nucleating agent in molten polypropylene. This phenomenon is called "self-nucleation" [17]. J. Breda Showed that using a nucleating agent leads to the formation of hexagonal spherulites (melting point = 152°C), which change to monoclinic (melting point = 165°C) during heat treatment [3]. The same author showed that phthalocyanine based pigments act as nucleating agents for polypropylene, leading to the formation of monoclinic form, while quinacrydine leads to hexagonal form. He also showed that as the spinning speed increased, there was more monoclinic and less hexagonal crystals produced. Then, he concluded that at high spinning speeds crystallization is mainly determined by

primary nucleation and nucleating agents play a lesser important role. Finally, J. Breda believes that in the absence of additives as nucleating agents, the oriented chain molecules act as nucleating agent [2, 3]

As literature review show a rather limited information exists on the nucleation effect of pigment dyes and most researchers have mainly concentrated on the nucleation of non-polypropylene fibres. Therefore, it is the aim of this research to carry out a thorough study on the nucleation effect of pigment dyes on the microstructure of coloured polypropylene fibers.

EXPERIMENTAL

Materials

In this research, polypropylene granulate from Tabriz Petrochemicals Co was used. The MFI value and melting point of these granulates were 16 and 170°C, respectively. The pigment dyes used were as follows:

- C.I. Pigment Yellow 83
- C.I. Pigment Red 48
- C.I. Pigment Blue 15
- C.I. Pigment Violet19
- C.I. Pigment Black 7
- C.I. Pigment White 6

Equipment

The equipment used in this research was as follows:

- Twin screw extruder (46 mm diameter, L/D = 44, Frester, Japan) for the production of master batch.
- Pilot spin-draw-texture (bulked continuous filament = BCF) line with a single screw extruder and two spinnerets each having 120 trilobal orifices.
- Polarizing light microscope with compensating system (Carl-Zeiss).
- Differential scanning calorimetry (DSC) (Perkin Elmer).
- Manual press for the preparation of samples for FTIR .
- BOMEM (MB100) FTIR Spectroscopie (Braun and Hartmann) for measuring the percentage crystallinity of the samples.
- Zwick tensometer (Model 1446) based on CRE method for measuring the tenacity of the samples.
- Testrite thermal shrinkage oven for measuring the thermal shrinkage of fibres.

Sample Production

Master batch samples which consisted of 65% polypropylene, 5% wax and 30% pigment dyes, were produced with the help of Frester twin screw extruder.

BCF yarns (1700 decitex and 120 filaments) with 2% pigment (relative to fibre weight) were produced with the help of the pilot spin-draw-texture (BCF) line with a speed of 1100 m/min. The temperature profile of the 5 heating zones and the filter of the single screw extruder was 205, 208, 212, 217, 222 and 228°C, respectively. The spinning pack had a temperature of 238°C. Draw ratio in the drawing zone was 4.5. The texturing conditions were as follows:

Hot air temperature: 130°C

Hot air pressure: 3 (bar = kgf/cm²)

Methods

Nucleation studies were carried out by polarizing microscope. For this analysis, the samples were dissolved in xylene at 125°C for 6 h. The solution was then heated at 128°C for 10 min. A few drops of the solution was laid on a glass, so that xylene evaporated and a thin polymeric film was formed. This film was heated for 15 min at 195°C to melt and then cooled to 120°C to crystallize for 30 min before the analysis started. Photographs were taken by the camera mounted on the microscope.

Melting and crystallization temperatures of the samples were measured by DSC. For DSC analysis, the samples of about 5 mg were left at 50°C for one min and subsequently heated to 300°C with a rate of 20°C per min. The samples were then cooled to room temperature with the same rate.

Percentage crystallinity of the BCF yarns for the purpose of comparison was calculated by dividing the crystalline peak intensity by the amorphous peak intensity obtained from FTIR spectrum. The specimen was prepared by mixing 1 part of the yarn in powder form with 100 parts KBr in the form of a thin film.

Birefringence of the samples was measured by compensation polarizing light microscope as follows:

The specimen was laid between the analyzer and polarizer (perpendicular to each other) at 45 degrees and the interfering lights were observed carefully. The quartz blade was used for the determination of the order of the colour due to phase lag. Finally, birefringence was obtained by measuring the fibre thickness and

using the information obtained from Michelle Levy interfering colours' table.

Tenacity of yarns was measured by Zwick tensometer according to ASTM: D2256-80. 30 Specimens were chosen for this test.

The thermal shrinkage of fibres was measured by a Testrite thermal shrinkage oven according to ASTM D 4974-93. 5 Specimens were chosen for this test[18].

RESULTS AND DISCUSSION

Spherulite Size and Form

Figure 1 shows the spherulites of uncoloured polypropylene and Figures 2 - 7 show the spherulites of coloured polypropylene.

Figures 2, 3 and 4 show that C.I. Pigment Yellow 83, Black 7 and Blue15 reduce the size and increase the number of spherulites in polypropylene. Attention is drawn to the fact that the extent of the effect of each pigment is somehow different i.e., Black 7 has a less pronounced effect when compared with Yellow 83 and Blue 15.

Kargin et al. [10] and Rybnikar [13] have related the reduction in size and the increase in the number of spherulites, as a result of adding additives, to their nucleating power, i.e. acting as crystallization nucleus. The nucleation effect of carbon black and C.I. Pigment Blue 15 has been reported by other researchers [3,4,6].

Figures 5-7 show that C.I. pigment Red 48, white 6 and Violet 19, in comparison to the other three pigment dyes do not reduce the size of the spherulites, however, they indicate a rather different spherulite form, when compared with uncoloured polypropylene. For pigment

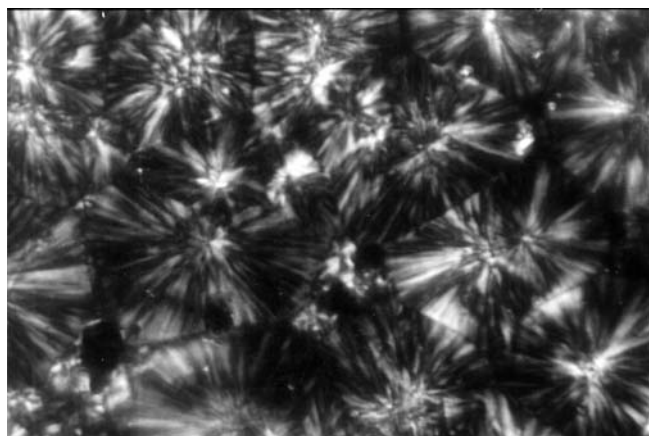


Figure 1. Spherulites of uncoloured polypropylene.

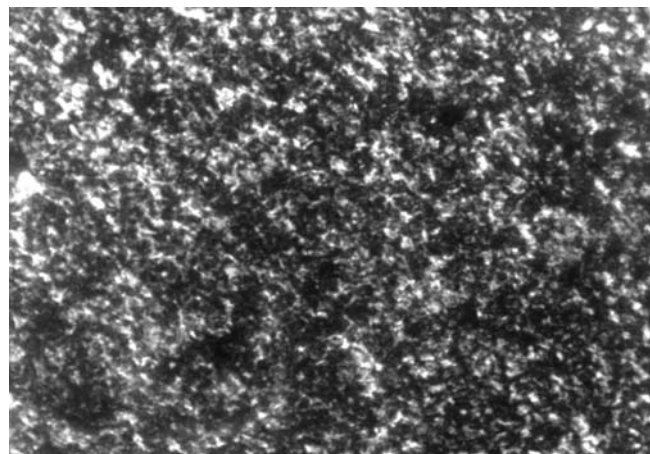


Figure 2. Spherulites of coloured polypropylene (C.I. Pigment Yellow 83, x200).

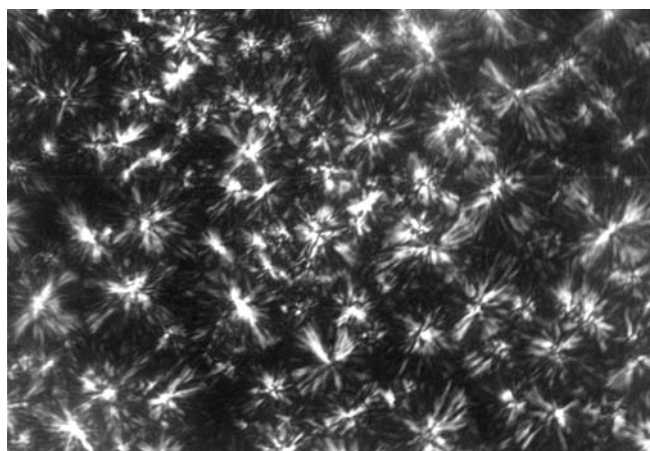


Figure 3. Spherulites of coloured polypropylene (C.I. Pigment Black 7, x200).

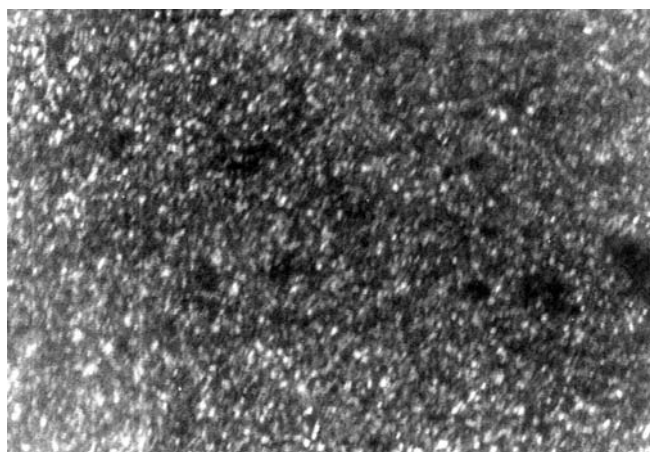


Figure 4. Spherulites of coloured polypropylene (C.I. Pigment Blue 15, x200).

White 6, even a slight increase in the size of the spherulites is observed. Similar results have also been

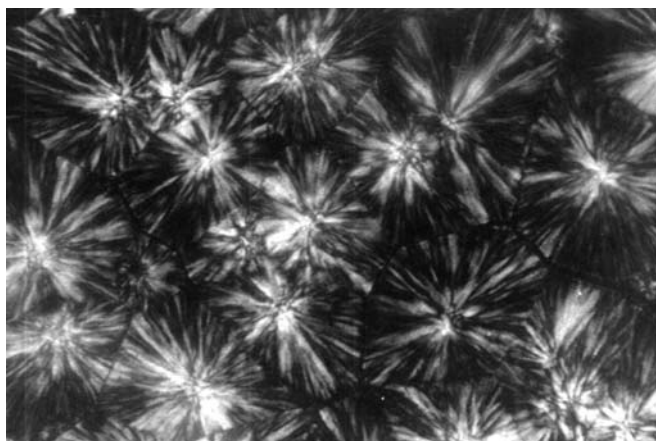


Figure 5. Spherulites of coloured polypropylene (C.I. Pigment Red 48, x200).

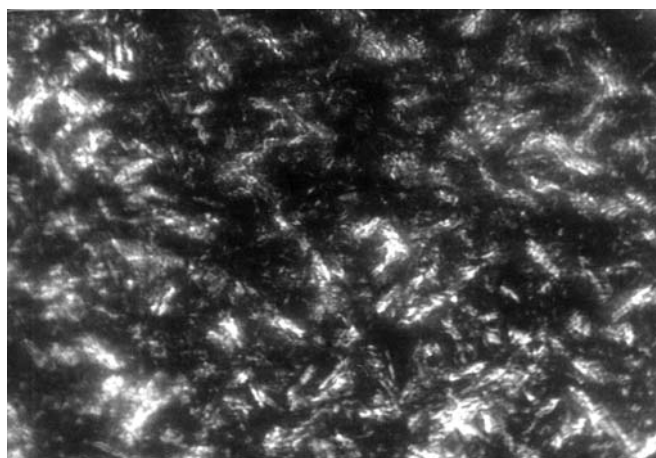


Figure 6. Spherulites of coloured polypropylene (C.I. Pigment Violet 19, x200).

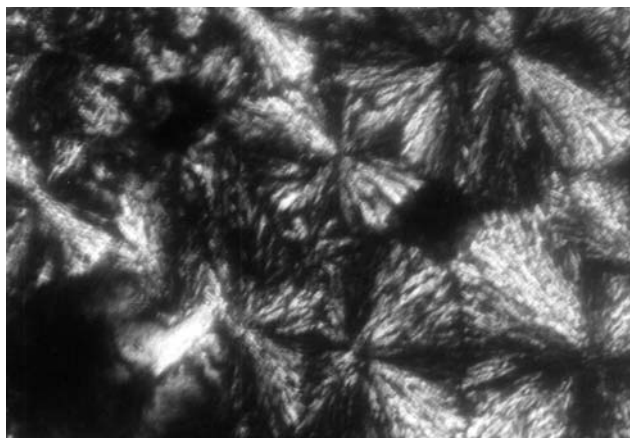


Figure 7. Spherulites of coloured polypropylene (C.I. Pigment White 6, x200).

reported by Broda [3] and Beck [11]. J. Broda has related this change to the formation of hexagonal crystalline form [3].

This study has shown that as far as the nucleation effect is concerned, pigment dyes act differently on polypropylene. Even, polypropylene from different sources may not show a similar spherulitic size and shape. This has also been observed by Rybnikar [13].

Crystallization and Melting Point

Figures 8 -21 show the DSC thermograms (cooling and heating) of uncoloured and coloured polypropylene fibres. Table 1 shows the crystallization temperature and melting points of uncoloured and coloured polypropylene fibres obtained from these figures. As it can be seen, the pigment dyes affect the crystallization temperature differently. In fact, those pigment dyes like Yellow 83 and Blue 15 that act as stronger nucleating agents would increase the crystallization temperature of polypropylene fibres even more. Higher crystallization temperature means, after leaving the spinneret,

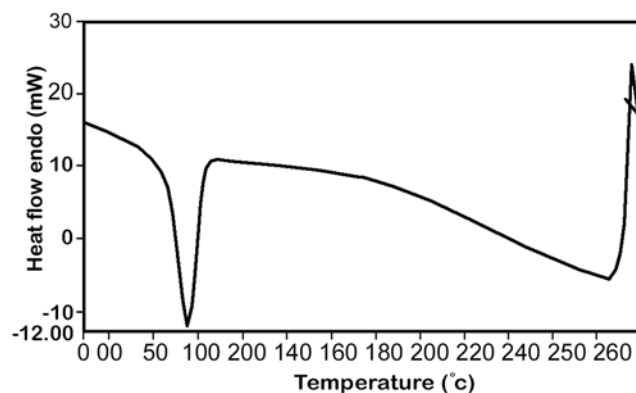


Figure 8. Thermogram of uncoloured polypropylene (cooling).

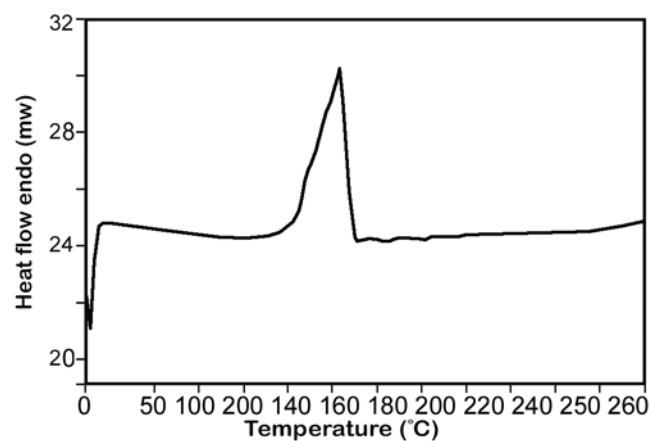


Figure 9. Thermogram of uncoloured polypropylene (heating).

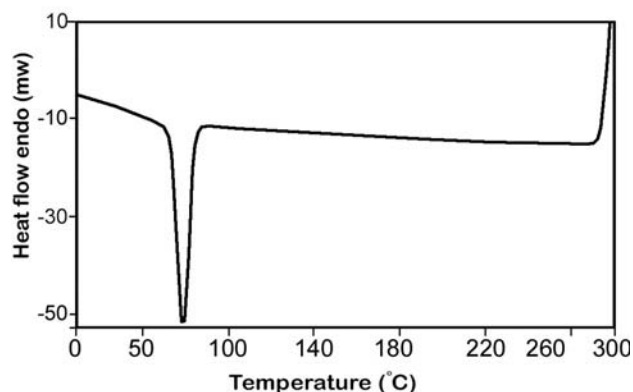


Figure 10. Thermogram of coloured polypropylene (C.I. Pigment Red 48) (cooling).

crystallization of the molten polymer starts at a higher temperature, in other words, at a shorter distance from the spinneret orifice. This affects the mechanical properties of fibres considerably.

Figure 9 shows that polypropylene melts at 164°C. Figures 13, 15 and 17 show Yellow 83, Black 7 and Blue 15 behave rather similar to uncoloured polypropylene, but as Table 1 shows, the Yellow 83 and Blue 15 increase the melting point of polypropylene by about 2.3 and 2.7°C, respectively, whereas, the Black 7 decreases the melting point by about 4°C. From Figures 11, 19 and 21 it can be seen that Red 48, Violet 19 and White 6 show a different behaviour, in that a rather sharp peak is not observed, but instead, two peaks with a considerable range characterize this behaviour. According to Table 1, the first peak of White 6 and Violet 19 is considerably lower than 164°C, whereas, their second peak is about 0.7°C lower than uncoloured polypropylene. For Red 48, there is a shift of about 6-

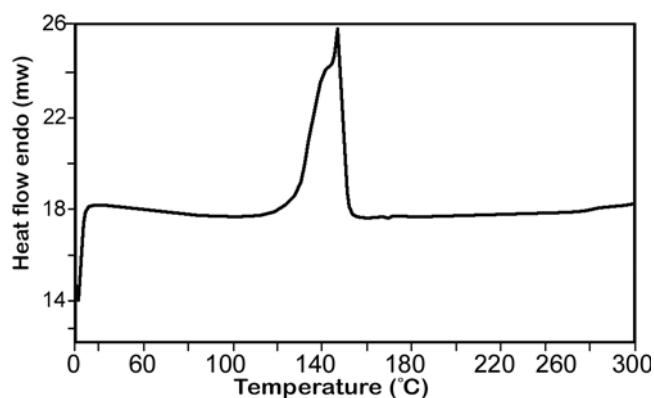


Figure 11. Thermogram of coloured polypropylene (C.I. Pigment Red 48) (heating).

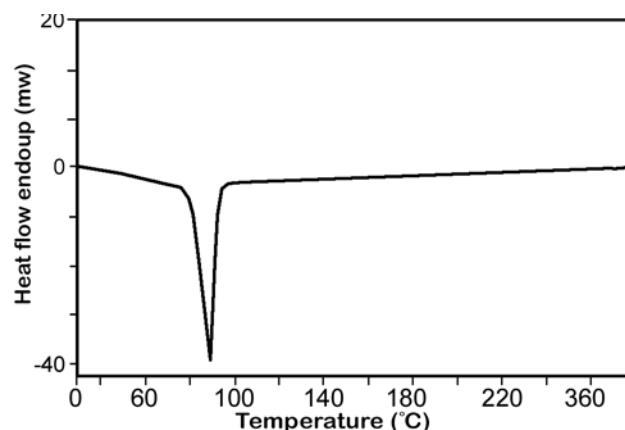


Figure 12. Thermogram of coloured polypropylene (C.I. Pigment Yellow 83) (cooling).

7°C namely, 163 and 168.7°C for the first and second peak, respectively.

Assuming that the characteristic sharp melting peak indicates the absence of a two phase system in the fine structure of polypropylene fibres, a monoclinic form is assumed for uncoloured, Yellow 83, Blue 15 and Black 7 coloured polypropylene BCF fibre. It is also concluded that Yellow 83, Blue 15 and Black 7 have the ability to act as monoclinic (α) nucleating agent. This is in accordance with the observations already made from Figures 2-4.

For Violet 19, White 6 and Red 48, it is concluded that they act as a hexagonal (β) nucleating agent and their employment in the molten polypropylene brings about the formation of a two phase system (hexagonal and monoclinic) for the mass dyed fibres which shows two melting peaks as observed in Figures 19 and 21.

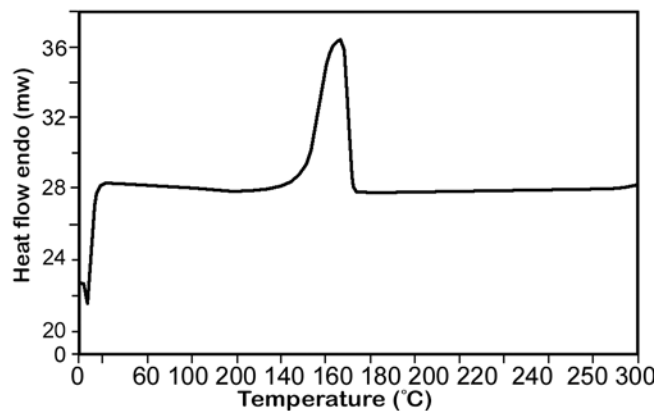


Figure 13. Thermogram of coloured polypropylene (C.I. Pigment Yellow 83) (heating).

Table 1. Crystallization and melting points of uncoloured and coloured BCF polypropylene fibres.

Melting point (°C)		Starting crystallization temperature (°C)	Crystallization temperature peak (°C)	C.I. Pigment
Second peak	First peak			
160	-	109.5	100	C.I. P Black 7
163.3	156	109.5	101.3	C.I. P White 6
163.3	157.3	111	100	C.I. P Violet 19
166.3	-	116	104.7	C.I. P Yellow 83
166.7	-	120	114	C.I. P Blue 15
168.7	163	106.5	98.7	C.I. P Red 48
164	-	107	95.4	Uncoloured PP

Percentage Crystallinity

Table 2 shows the percentage crystallinity, amorphous peak intensity and crystalline peak intensity of uncoloured and mass dyed BCF polypropylene calculated from the FTIR spectra. As it can be seen, with the exception of Red 48, all other pigment dyes, acting as nucleating agent increase the percentage crystallinity of the polypropylene fibres. As Red 48 reduces the percentage crystallinity slightly, it may be concluded that the nucleation effect of Red 48 may be negligible. Wlochowicz [6] believes that non-nucleating agents do not have the ability to increase the orientation of molecular chains and form lamella system.

Birefringence

Table 3 shows the birefringence values of the BCF fibres. As it can be seen the mass dyed fibres have a lower birefringence value than the uncoloured fibre. It

Table 2. Percentage crystallinity, amorphous peak intensity and crystalline peak intensity of uncoloured and coloured BCF polypropylene.

C.I. Pigment	Crystalline peak intensity	Amorphous peak intensity	Crystallinity (%)
Violet 19	0.039	0.044	88.14
Yellow 83	0.072	0.082	87.92
White 6	0.054	0.062	87.06
Blue 15	0.070	0.080	86.72
Black 7	0.042	0.049	85.81
Red 48	0.029	0.035	83.12
Uncoloured PP	0.028	0.033	84.78

is interesting to note that the effect on reducing the birefringence value of pigments with monoclinic nucleation capability, namely, Yellow 83, Blue 15 and Black 7 is more pronounced than the pigments with hexagonal nucleation capability. This may be due to the fact that the pigments somehow put up some resistance against the overall orientation. Generally speaking, the reduction in birefringence of mass dyed fibres can be related to the fact that, crystallization at higher temperature means crystallization at lower stresses, and lower stresses lead to a lower overall orientation.

Tenacity

Table 4 shows that mass dyed fibres have a lower tenacity than uncoloured fibre. It is pointed out that tenacity is dependent on the percentage crystallinity and the overall orientation of the fibre. Attention is drawn to the fact that, apart from the morphology of mass dyed fibres, the size and distribution of pigment dyes in mass dyed fibres can affect their mechanical

Table 3. Birefringence of uncoloured and coloured BCF polypropylene.

C.I. Pigment	Birefringence
C.I. Pigment Yellow 83	0.016
C.I. Pigment Blue 15	0.017
C.I. Pigment Black 7	0.019
C.I. Pigment White 6	0.020
C.I. Pigment Violet 19	0.023
C.I. Pigment Red 48	0.023
Uncoloured PP	0.026

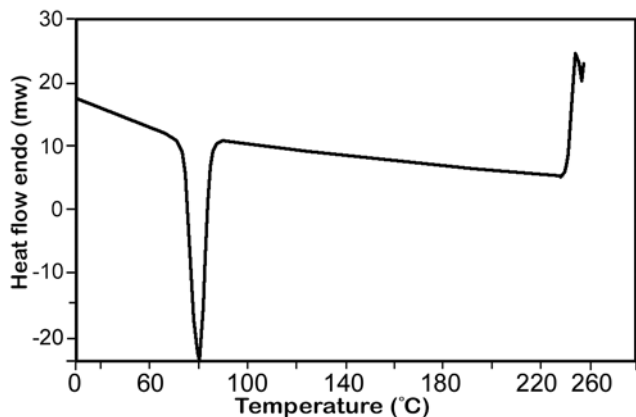


Figure 14. Thermogram of coloured polypropylene (C.I. Pigment Black 7) (cooling).

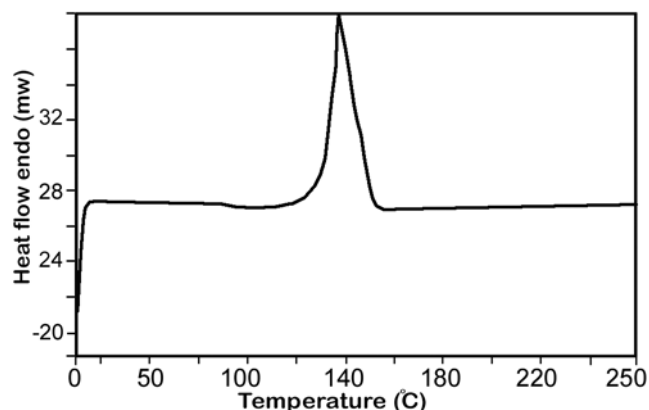


Figure 15. Thermogram of coloured polypropylene (C.I. Pigment Black 7) (heating).

properties. From Tables 2-4, it can be concluded that the reduction in overall orientation as a result of adding pigment dyes has a more negative effect than the possible positive effect of the increase in crystallinity.

Table 4. Tenacity of uncoloured and coloured BCF polypropylene.

C.I. Pigment	Tenacity (cN/tex)
C.I. Pigment Yellow 83	15.28(0.63)
C.I. Pigment White 6	15.98(1.30)
C.I. Pigment Black 7	16.59(0.56)
C.I. Pigment Blue 15	17.23(0.86)
C.I. Pigment violet 19	18.14(0.45)
C.I. Pigment Red 48	18.86(1.37)
Uncoloured PP	19.53(0.68)

N.B.: Numbers in the brackets show the standard deviation.

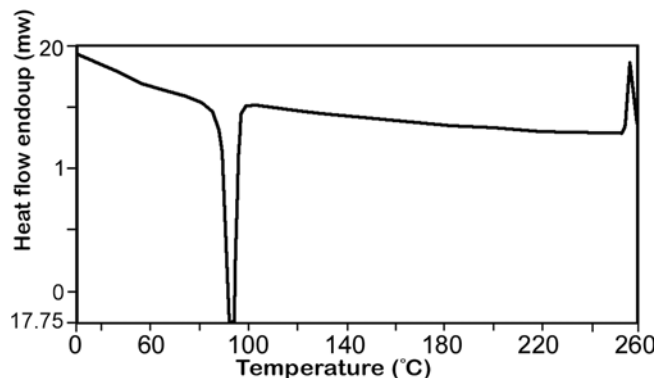


Figure 16. Thermogram of coloured polypropylene (C.I. Pigment Blue 15) (cooling).

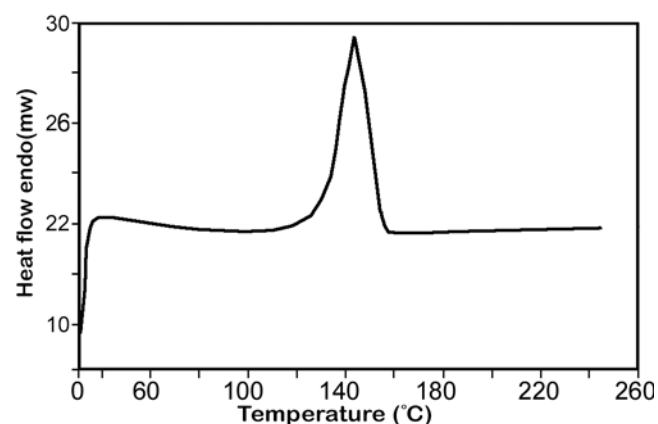


Figure 17. Thermogram of coloured polypropylene (C.I. Pigment Blue 15) (heating).

Thermal Shrinkage

Table 5 shows the percentage shrinkage of BCF polypropylene at 110, 120 and 130°C. As it can be seen almost in all cases, pigment dyes reduce the thermal shrinkage of fibres. This is in accordance with Gupta et al. [19, 20], reporting that increase in crystallinity, reduction in birefringence (lower overall orientation) and less hexagonal form, lead to a lower thermal shrinkage. The increase in crystallinity and reduction in birefringence of mass dyed fibres have already been discussed. Table 5 shows that Yellow 83, Blue 15 and Black 7 with their monoclinic nucleation capability reduce the thermal shrinkage of BCF fibres more than Violet 19 and Red 48 with hexagonal nucleation capability. White 6 with hexagonal nucleation capability has the biggest effect on the reduction of thermal shrinkage. It is also obvious that at higher temperatures, the shrinkage increases. This is due to the fact that, higher

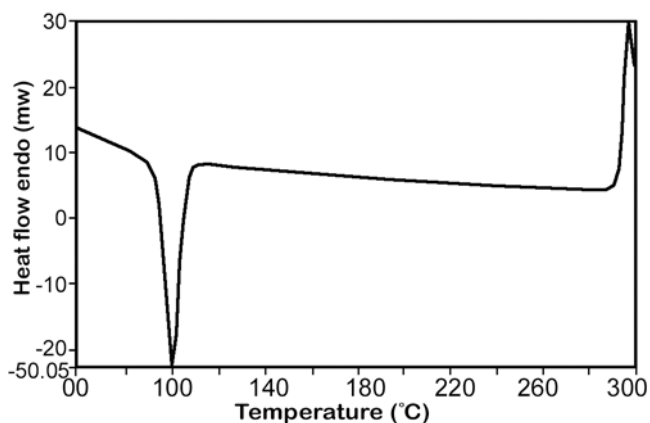


Figure 18. Thermogram of coloured polypropylene (C.I. Pigment violet 19) (cooling).

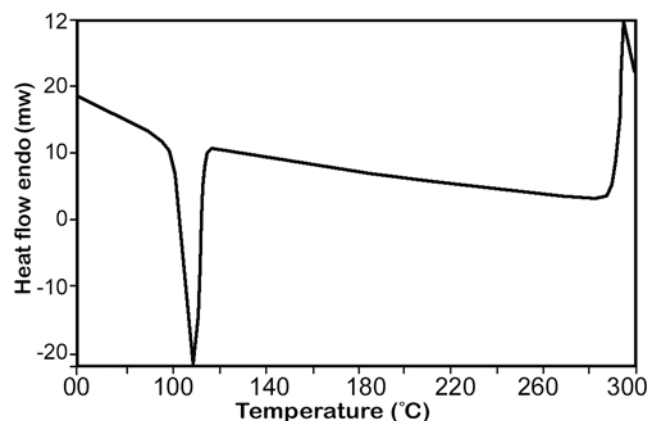


Figure 21. Thermogram of coloured polypropylene (C.I. Pigment White 6) (heating).

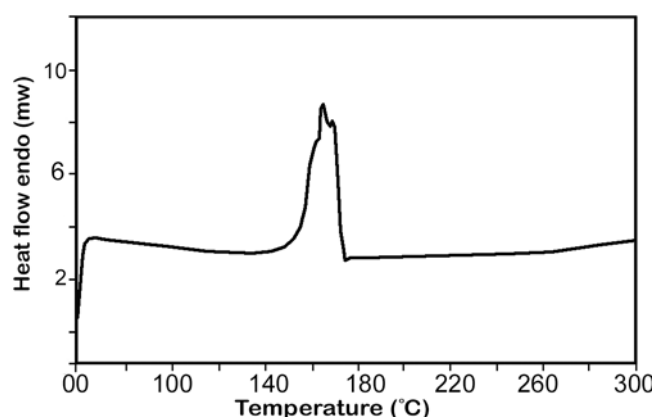


Figure 19. Thermogram of coloured polypropylene (C.I. Pigment Violet 19) (heating).

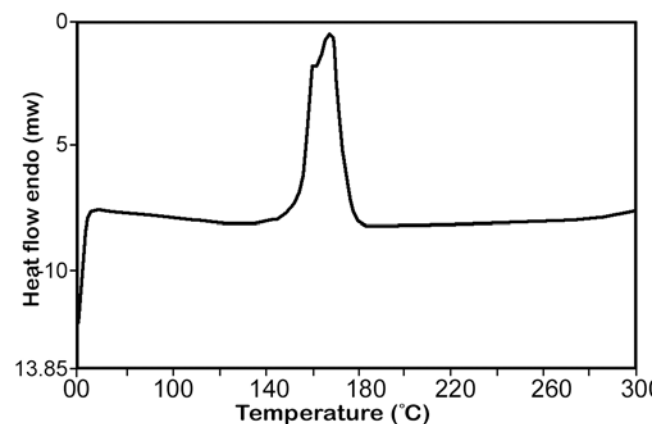


Figure 20. Thermogram of coloured polypropylene (C.I. Pigment White 6) (cooling).

relaxation temperatures provide higher amount of energy and hence more stress is relieved, i.e. higher shrinkage [19, 20].

Table 5. Percentage thermal shrinkage of uncoloured and coloured BCF polypropylene.

C.I. Pigment	110	120	130
	(°C)		
White 6	0.00	0.20	0.90
Black 7	0.00	0.37	1.41
Yellow 83	0.27	1.30	1.80
Blue 15:3	0.30	1.50	2.30
Red 48	0.40	1.80	3.13
Violet 19	0.55	2.15	3.86
Uncoloured PP	0.48	2.21	4.70

CONCLUSION

The results showed that

- C.I. Pigment Yellow 83, Black 7 and Blue15 reduce the size and increase the number of spherulites of the polypropylene according to their nucleation capability. C.I. pigment Red 48, White 6 and Violet 19 do not reduce the size of the spherulites.

- Pigment dyes that act as a stronger nucleating agents increase the crystallization temperature of polypropylene fibres more.

- C.I. Pigment Yellow 83, Blue 15 and Black 7 act as monoclinic (α) nucleating agent. C.I. Pigment Violet 19, White 6 and Red 48 act as hexagonal (β) nucleating agent and their presence in the molten polypropylene leads to a two phase system.

- All pigment dyes with the exception of Red 48 increase the percentage crystallinity of the polypropy-

lene fibres. Red 48 reduces the percentage crystallinity slightly.

- All pigment dyes lower the birefringence value of the uncoloured fibre. Pigment dyes with monoclinic nucleation capability, show a more pronounced effect than the pigments with hexagonal nucleation capability.

- The reduction in overall orientation as a result of adding pigment dyes to polypropylene fibres leads to a lower tenacity for mass dyed fibres.

- Mass dyeing with pigment dyes reduces the thermal shrinkage of fibers. As a result of higher crystallinity and lower birefringence, mass dyeing leads to a lower thermal shrinkage.

ACKNOWLEDGEMENTS

The authors wish to thank Mr Hossein Ghazvini (Eng.), Managing Director of Pars Polypropylene Co. (Isfahan, Iran) for the technical assistance. Furthermore, they are also grateful to Mrs A. Ataian (Eng.) and Mr M. Sedighipour (Eng.) for their assistance.

REFERENCES

- Ahmed M., Polypropylene fibers Science and Technology, Elsevier, 641-648 (1988).
- Broda J., Wlochowicz A., Influence of pigment on supermolecular structure of polypropylene fibers, *Eur. Polym. J.*, **36**, 1283-1297 (2000).
- Broda J., Morphology of the noncolored and colored polypropylene fibers, *Polymer*, **44**, 1619-1629 (2003).
- Nakafuku C., High pressure DTA study on the melting and crystallization of isotactic PP, *Polymer*, **22**, 1673-1676 (1981).
- Edenbaum J., Plastic Additives and Modifiers Handbook, Plastic Industry Consultant, New York, Van Nostrand, Reinhold, 638-912 (1992)
- Wlochowicz A., Broda J., Slusarczyk C., X-Ray structural investigation of polypropylene fibers dyed in the melt with organic pigment dyes, *Acta Polym.*, **40**, 95-98 (1989).
- Harkin-Jones E., Murphy W.R., Macauley, *Colouring Technology for Plastics*, SPE, Norwich, USA, 249-254 (1999).
- Spruiell J.E. (Salem Ed.). Structure formation in polymeric fibers. Munich: Carl Hanser, 29-50 (2001).
- Kargin V.A., Pashinin B.P., Effect of structurizing agents on the properties of polyolefins, *Vysokomol. soyed.*, **8**, 2318-2325 (1966).
- Kargin V.A., Sogolova T., Rapoport N., Effect of artificial nucleating agent on polymer structure and properties, *J. Polym. Sci.*, Part C, 1609-1617 (1967).
- Beck H.N., Heterogeneous nucleating agents for polypropylene crystallization, *J. Appl. Polym. Sci.*, **11**, 673-685 (1967).
- Binsbergen F.L., Heterogeneous nucleation in crystallization of polyolefins, *J. Polym. Sci., Polym. Phys.*, **11**, 117-135 (1973).
- Rybnikar F., Efficiency of nucleating additives in polypropylene, *J. Appl. Polym. Sci.*, **13**, 827-833 (1969).
- Sogolova T.A., Kurbanova, Structure formation in polypropylene in the melt in the presence of artificial nucleating agents, *Vysokomol. soyed.*, **8**, 1442-1443 (1966).
- Chatterjee A.M., Price F.P., Heterogeneous nucleation of crystallization of high polymers from the melt, *J. Polym. Sci. Pol. Phys.*, **13**, 2369-2383 (1975).
- Cramez M.C., Oliveira M.J., Effect of pigmentation on microstructure and properties of rotationally nolded polyethylene, *J. Mat. Sci.*, **33**, 4869-4877 (1998).
- Xiyuan Z., Yongin L., Crystallization behavior of partially melting polypropylene, *Polymer*, **42**, 9217-9222 (2001).
- Standard test method for thermal shrinkage of yarn and cord using the thermal shrinkage oven, ASTM D4974-93.
- Gupta V.B., Bhuvanesh Y.C., Studies on shrinkage characteristics of yarns made from polypropylene and polypropylene containing 5% polystyrene, *Ind. J. Fib. & Tex. Res.*, **21**, 167-178 (1996).
- Gupta V.B., Kedia, H., Huiligal S.R., Shrinkage characteristics of PET, nylon-6 and polypropylene yarns, *Ind. J. Fibre & Tex. Res.*, **21**, 101-108 (1996).